XPCS and the Nanoscale Dynamics in Glassy Colloidal Systems

Tracking the particle-scale motion in
out-of-equilibrium and aging systems

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X-ray Photon Correlation Spectroscopy

Dynamic Light Scattering with X-rays

- Scattering of a Coherent Source $\longrightarrow$ Speckle

- Autocorrelation of Intensity…

$$g_2(\vec{Q},t) = \frac{\left\langle I(\vec{Q},t')I(\vec{Q},t'+t)\right\rangle}{\left\langle I(\vec{Q},t')\right\rangle^2}$$

…Gives Dynamic Structure Factor:

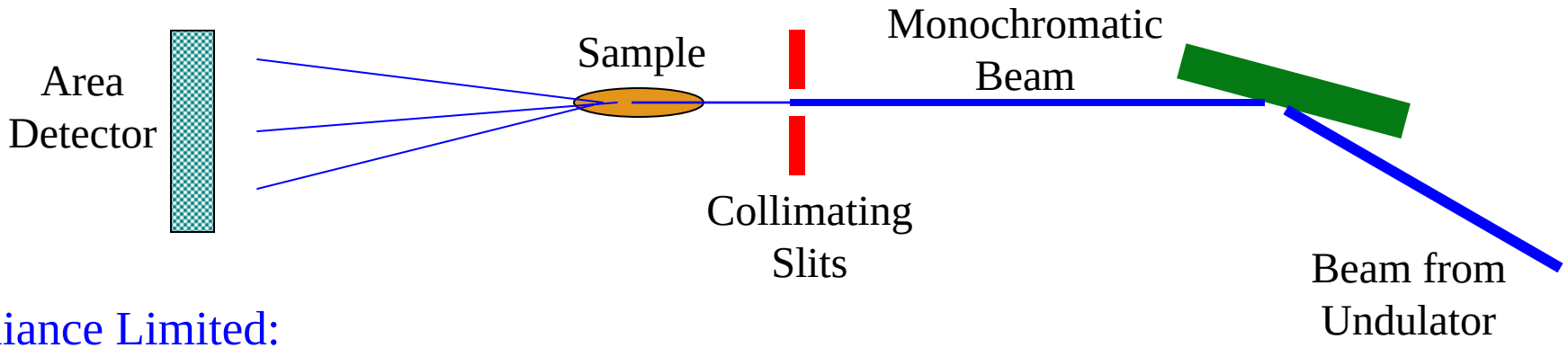
$$g_2(\vec{Q},t) = 1 + \beta\left[\frac{S(\vec{Q},t)}{S(\vec{Q},0)}\right]^2$$

$Co_{0.6}Ga_{0.4}$

QuickTime™ and a
GIF decompressor
are needed to see this picture.

G. Vogl, Universität Wien

Generating the coherent beam:



Brilliance Limited:

Transverse coherence length:

$\xi = \lambda R/2\pi\sigma \sim 10\ \mu m$

- Slit Aperture $\lesssim \xi$

source to sample distance: $R \sim 50$ m

x-ray wavelength: $\lambda \sim 1$ Å

source size: $\sigma \sim 100\ \mu m$

Longitudinal coherence length:

$\Lambda = \lambda\pi^{-1}(E/\Delta E)$

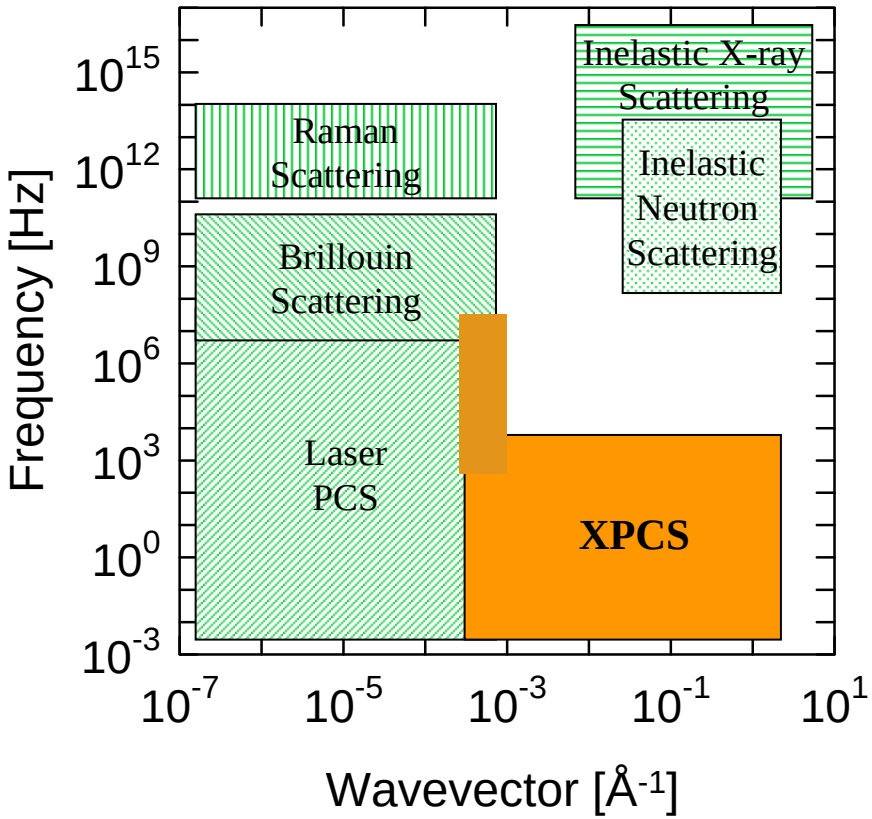
- Path Length Variation $\lesssim \Lambda$

spectral width: $(\Delta E/E) \sim 10^{-4}$

Statistical Uncertainty:

- S/N ~ 1/counts

Unique Realm of Dynamic Phase Space

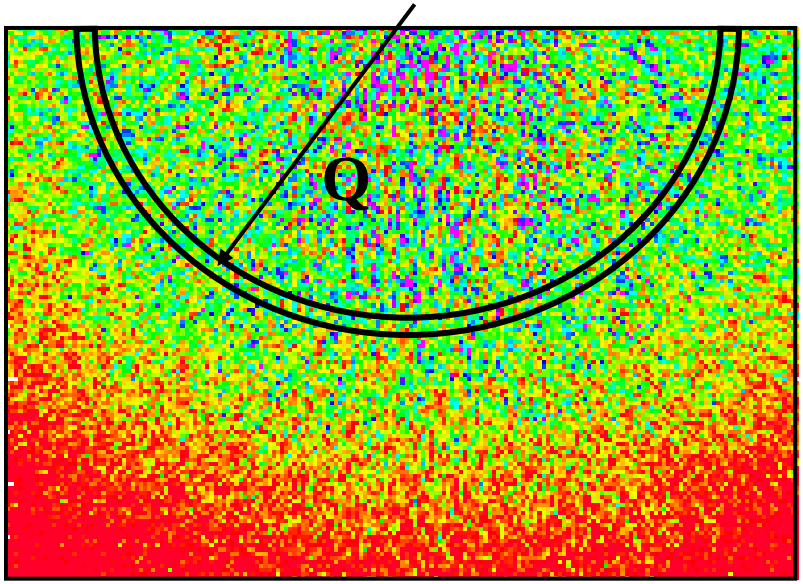


Is overlap with Neutron Spin Echo (NSE) Achievable?

Maximum NSE delay time ~ 100 ns.

Multispeckle XPCS

Average over Pixels = Ensemble Average



- Important for Weak Scatterers
- Crucial for Non-Ergodic Systems

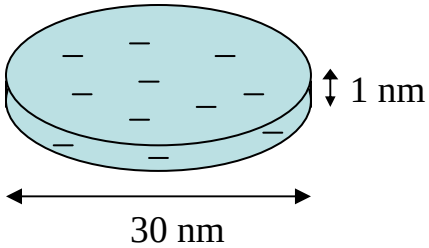
  e.g., Glasses, Gels

  Example: Clay Suspensions

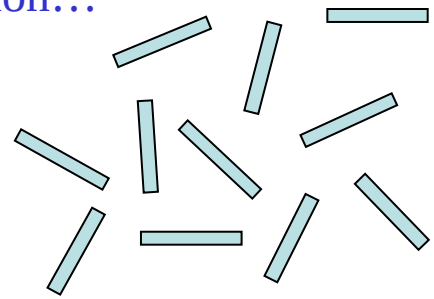
- **Demanding Tolerances for Area Detector!**
  - Throughput (Time Resolution)
  - Spatial Resolution
  - Quantum Efficiency

Laponite: A Synthetic Clay.

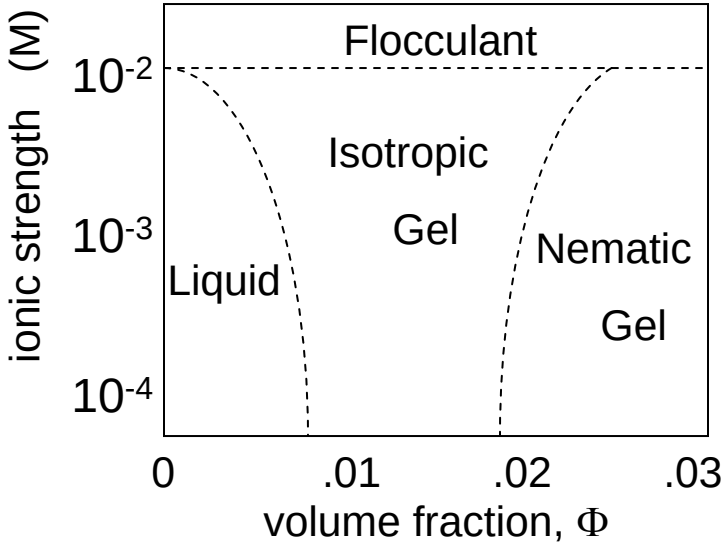
Charged Disks…



…in Aqueous Suspension…

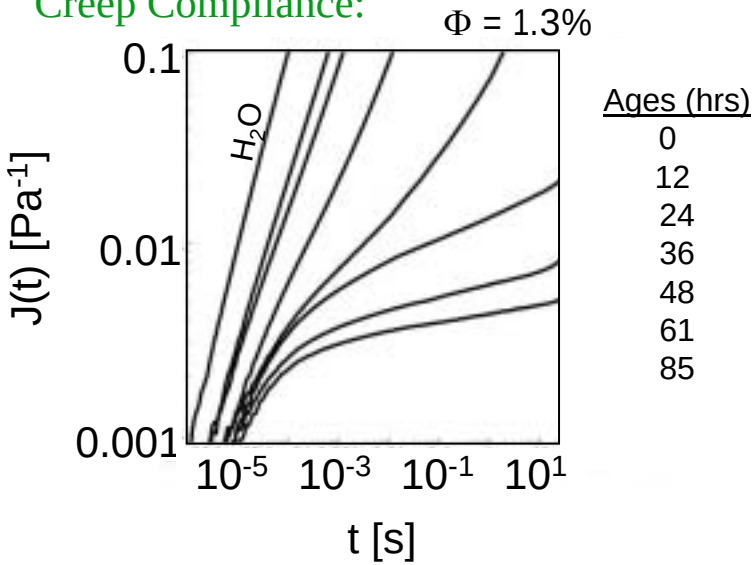


…Form Soft Solids…



…Over the Course of Hours or Days.

Creep Compliance:



- Can we probe the particle dynamics during this process?

Yes, with XPCS…

XPCS: Probe of the Local Dynamics.

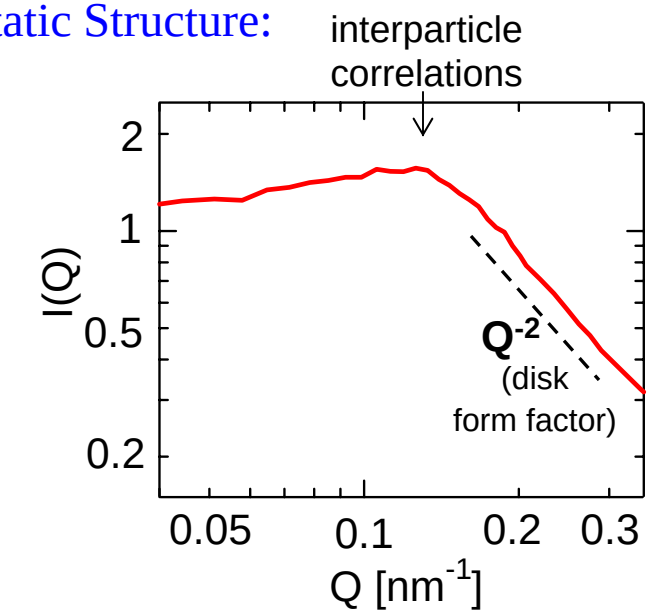
Sector 8-ID , APS

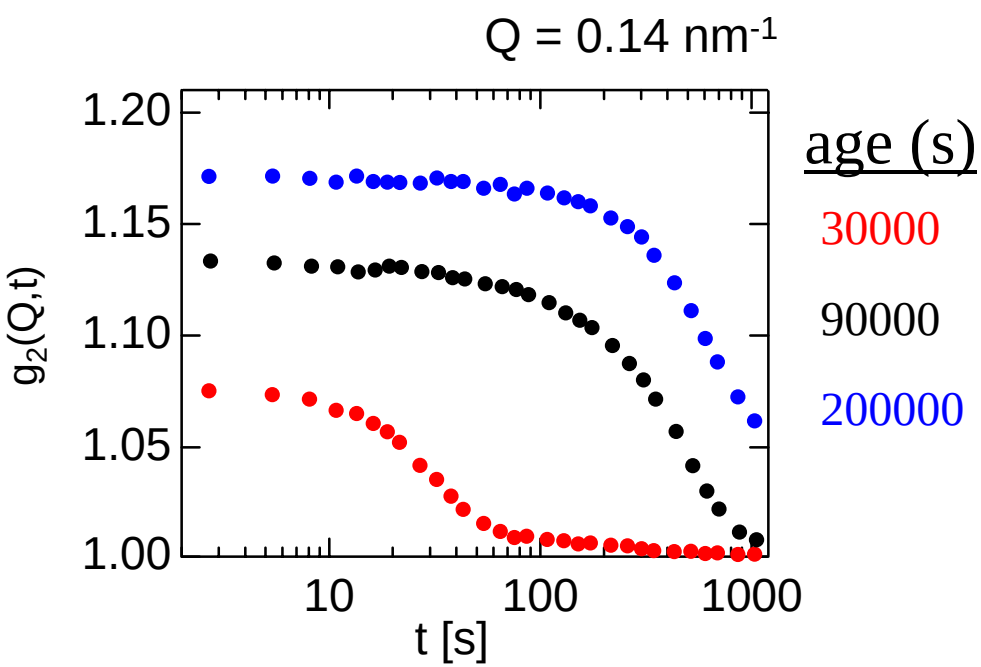
Over Wave Vector Range:

$0.03\ nm^{-1} < Q < 0.3\ nm^{-1}$

Motion Progressively Slows

Static Structure:





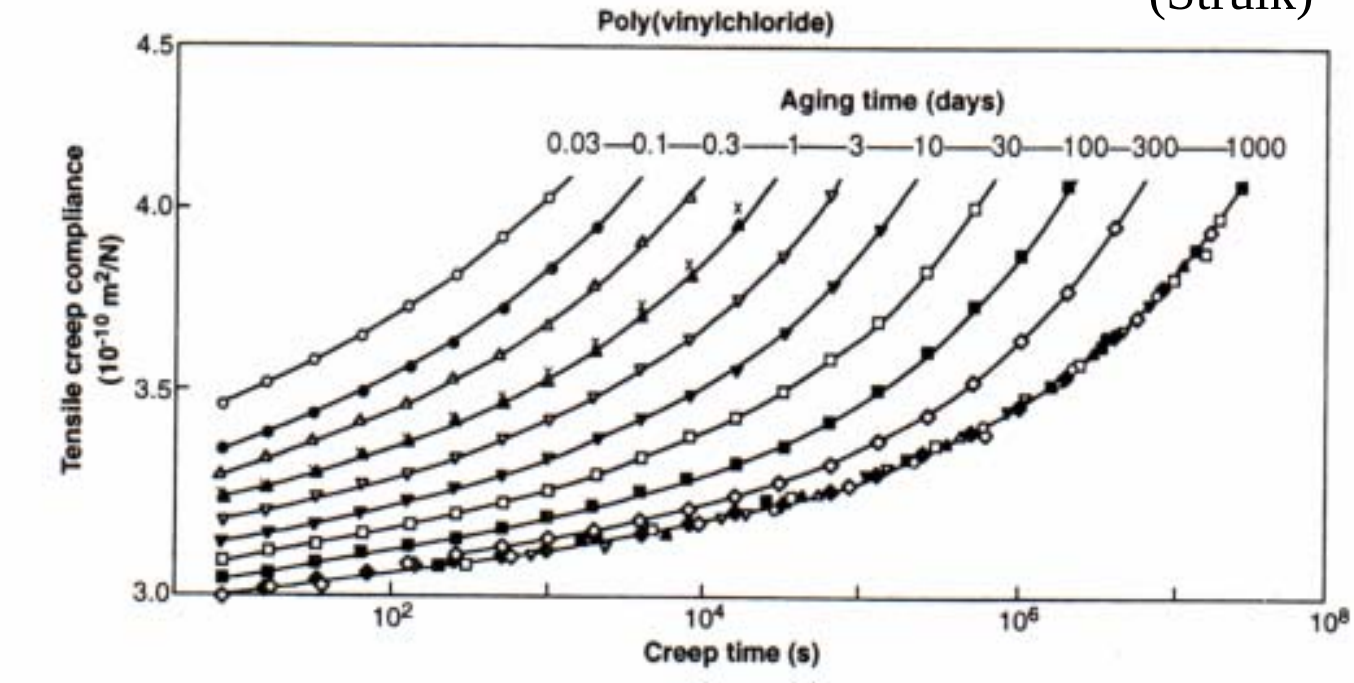
Correlations Fit to:

$$g_2(t) = A\exp\left[-\left(t/\tau\right)^{\beta}\right]+1$$

“Classic” Aging Behavior:

Eg., Creep compliance of polymer melts below T_g.

(Struik)

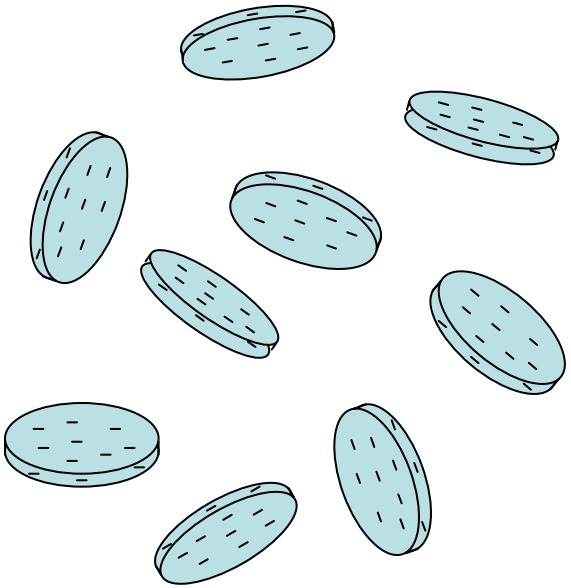


$$\tau = C\, t_a$$

However, for Particle-Scale Dynamics:

Glasses	$C > 10^3$
Clay Gel:	$C < 10^{-2}$

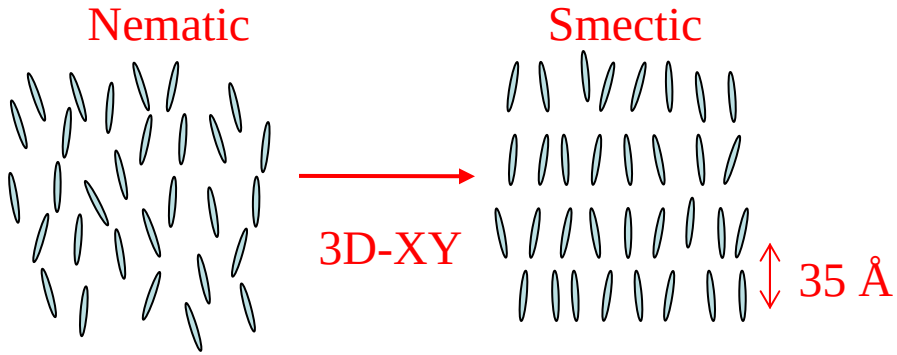
What Causes Stress in Laponite?



System evolves gently from liquid to solid…

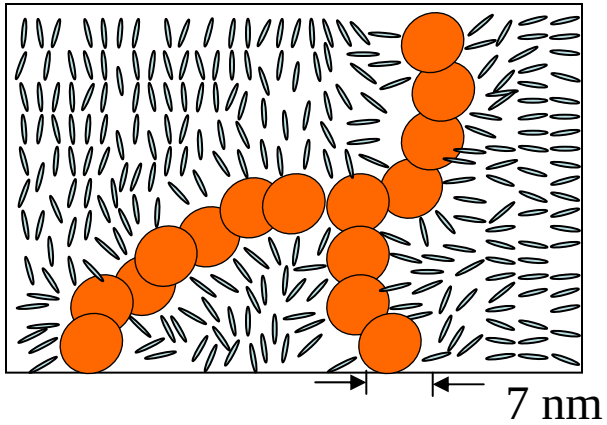
Smectic Liquid Crystals in Colloidal Gels

The smectic transition:



In a random environment:

H-bonded aerosil gel



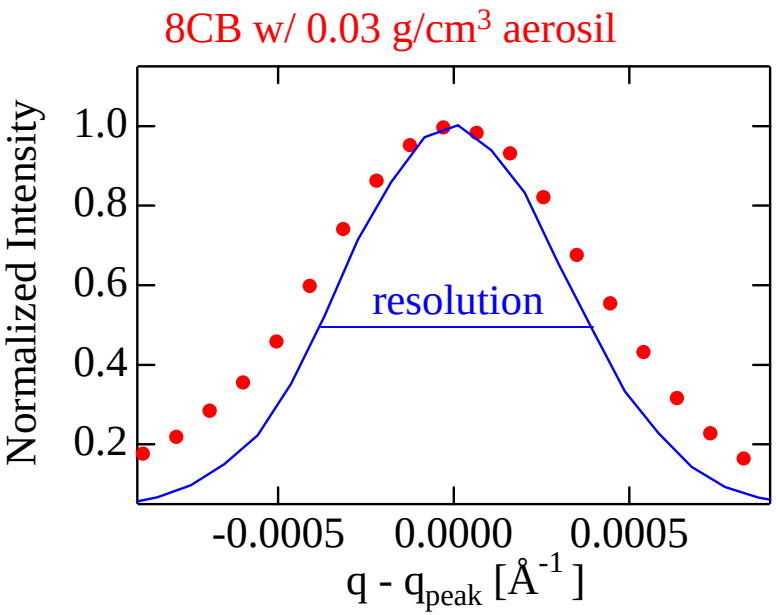
What is effect of quenched disorder?

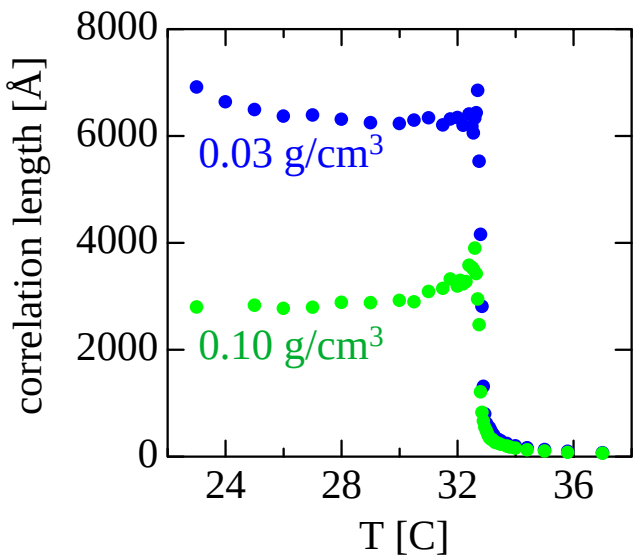
Transition Destroyed:

No thermodynamic signatures

Smectic correlations remain short ranged

X-ray Smectic Bragg Peak:



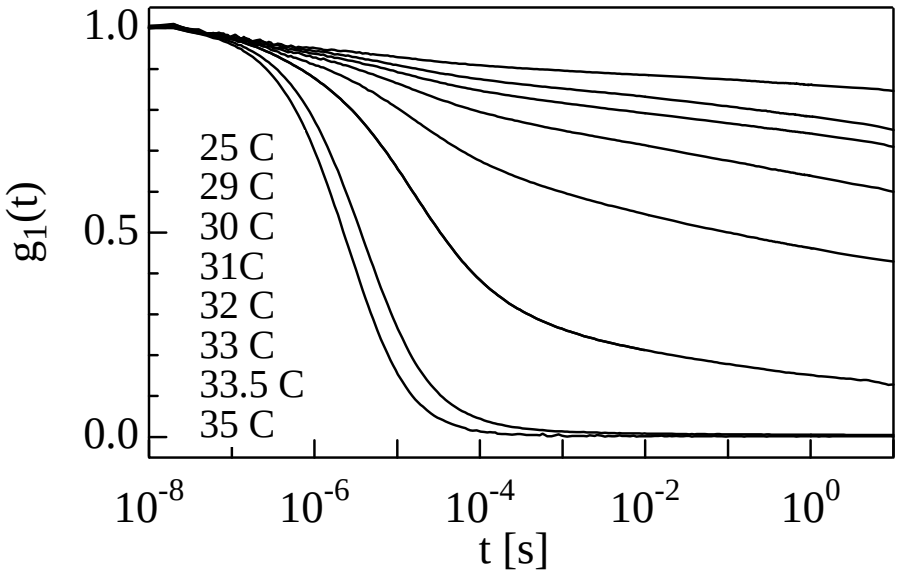


Smectic Peak Lineshape: Characteristic of Random-Field Induced Fluctuations.

Glassy Behavior of Smectic 8CB in Aerosil Gels:

Dynamic Light Scattering (DWS)

- Probes nematic fluctuations
- Observes dramatic slowing with onset of smectic order

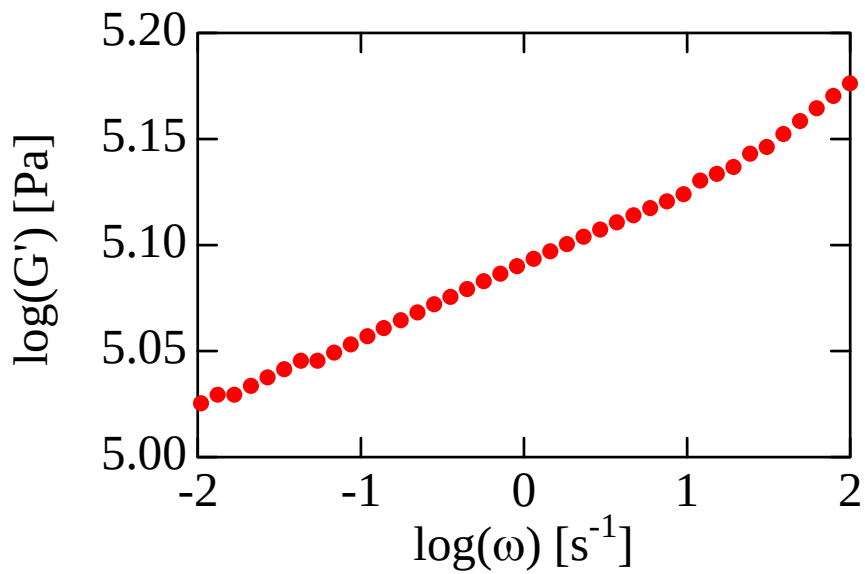


Rheometry

- Probes mechanical response
- Observes broad spectrum of relaxation times

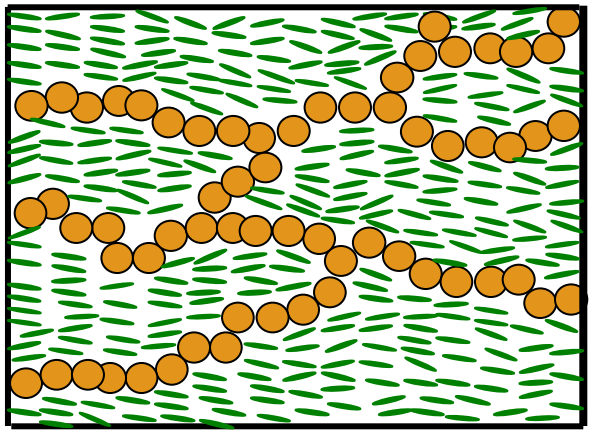
shear modulus:

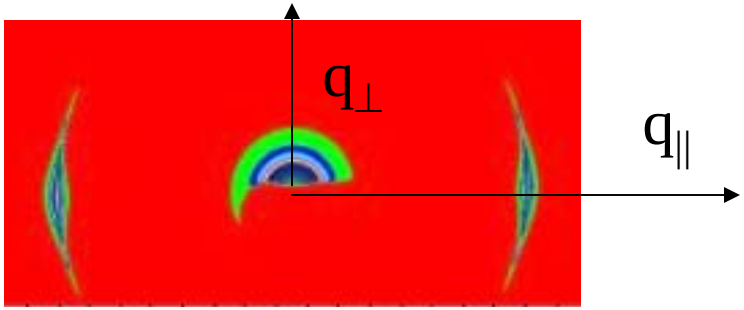
$$G'(\omega) \sim \omega^{0.1}$$



Decoupling nematic and smectic random fields:

Smectics in anisotropic gels





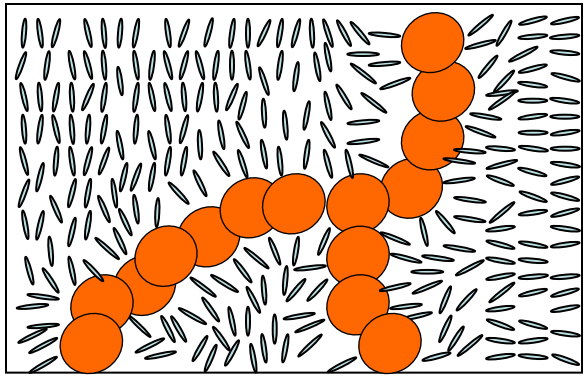
Predictions of Bragg Glass Phase

Strong scattering for XPCS

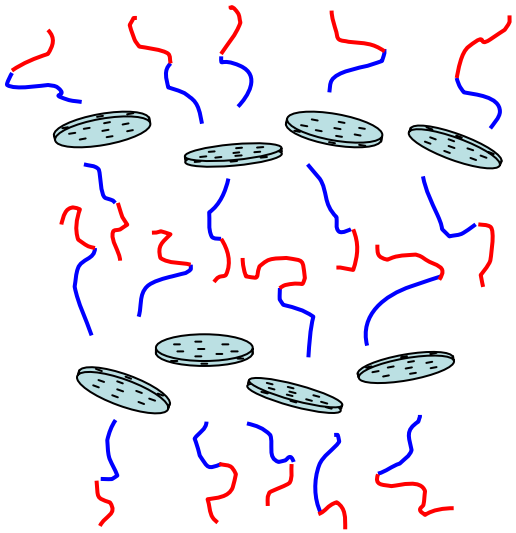
Future Directions of our Research:

XPCS as Probe of "Soft Glassy Materials".

eg., Nanocomposites:



Colloid + liquid crystals



Polymer + Clay

Objectives:

Connection between Glassy Rheology and Particle-Scale Dynamics.

Microscopic Perspective on Aging.

Need: High Throughput Area Detectors!